The Preparation and the Structure of Bis(1,3-dimethylureido)methane

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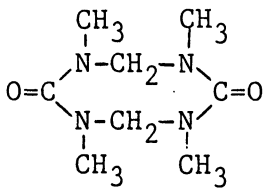
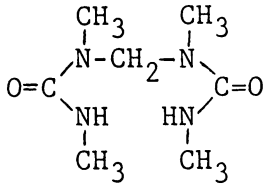
Synopsis. A new 1,3-dimethylurea-formaldehyde condensate, bis(1,3-dimethylureido)methane, was prepared and the molecular structure, as determined by X-ray analysis, and possible specific interaction to alkaline metal ions were compared with those of 1,3,5,7-tetramethyltetrahydro-1,3,5,7-tetrazocine-2,6(1*H*,3*H*)-dione. Although both structures are different from each other, their UV spectra in aqueous solution show that alkaline metal ions, Li^+ and Na^+, are caught by both of them.

In a previous paper,[1] 1,3,5,7-tetramethyltetrahydro-1,3,5,7-tetrazocine-2,6(1*H*, 3*H*)-dione (tetramethyldimethylenediurea: TMDMU) was reported to have a hole of 0.5—1.6 Å in the interior of the ring structure. When TMDMU was added to an aqueous solution of the lithium or sodium salt of phenol, a discernible shoulder at 225 nm characteristic to alkaline metal salts of phenol disappeared and the absorption spectrum in the UV region changed to that of phenol.[1]


(TMDMU)


(BDMUM)

A new 1,3-dimethylurea-formaldehyde condensation product, bis(1,3-dimethylureido)methane (BDMUM), was prepared and its molecular structure was determined by X-ray analysis. Possible specific interactions to alkaline metal ions in aqueous solution were compared with those of TMDMU.

Experimental

The Preparation of BDMUM. Ten grams of 1,3-dimethylurea were dissolved in 23.5 g of formalin and the pH of the solution was adjusted to 8.8 by successive additions of 20% NaOH aqueous solution. The reaction was carried out at 50 °C for 30 min. The reaction solution was evaporated to dryness under reduced pressure at 18—25 °C. A few ml of concd HCl was added as an acid catalyst to the desiccated residue in a large excess of MeOH. Keeping the temperature of the solution at 0—5 °C for 30 min, the reaction solution was neutralized with 20% NaOH aqueous solution at below −15 °C. After evaporation of the solvent, the methoxymethylated products were extracted with CH_2Cl_2, then with diethyl ether. After a viscous solution was evaporated under reduced pressure, the residue was distilled at 95—99 °C/1—2 Torr (1 Torr=133.322 Pa) to give 1-methoxymethyl-1,3-dimethylurea (yield 71%).

As an acid catalyst, 100 mg of *p*-toluenesulfonic acid was added to a mixture of 5 g of 1-methoxymethyl-1,3-dimethylurea and 3.3 g of 1,3-dimethylurea. The mixture was stirred for 30 min at 110 °C using an oil bath. Upon cooling, deposited white crystals were separated by filtration. Recrystallization from CH_2Cl_2 gave white rod-like crystals (Yield 82%), mp 145.0—146.2 °C. BDMUM was assigned by elemental analysis, ^1H and ^{13}C NMR and FD-MS spectrometry. ^1H and ^{13}C NMR spectra were measured in a $CDCl_3$, with TMS as the internal standard, at 90 MHz on a JEOL FX90Q instrument. Found: C, 44.57; H, 8.60; N, 29.72%: Calcd for $C_7H_{16}N_4O_2$: C, 44.68; H, 8.51; N, 29.79%: ^1H NMR, δ=6.32 (2H, q, J=4Hz, -NH-), 4.79 (2H, s, -CH_2-), 3.00 (6H, s, -CH_3), 2.78 (6H, d, J=4.5 Hz, -CH_3): ^{13}C NMR, δ=159.47 (>C=O), 63.07(-CH_2-), 34.90 (-CH_3), 27.50 (-CH_3): MS(FD); m/z=188(M^+).

X-Ray Analysis. A colorless single crystal with dimensions of ca. 0.1×0.2×0.2 mm^3 was mounted on a Rigaku AFC-6S diffractometer. The lattice parameters were determined by least-squares from 18 reflections in the 2θ range 20—30°. Systematic absences $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd. Intensity data were measured by means of the ω-2θ scan mode (scan speed 4° min^{-1} in ω) up to 2θ of 45° by using graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å). A deterioration of the crystal was not observed during measurements. Lorentz and polarization corrections were made, but no correction was made for absorption. 1008 independent reflections with $|F_o|>3\sigma$ ($|F_o|$) were used for a structure determination.

Crystal data for $C_7H_{16}N_4O_2$: M.W.=188.23, orthorhombic, space group Pbca, a=14.350(5), b=12.115(4), c=12.015(5) Å; V=2089(1) Å^3; Z=8; D_m=1.199, D_c=1.197 g·cm^{-3}; μ(Mo $K\alpha$)=0.9 cm^{-1}.

The structure of BDMUM was solved by a direct method (MULTAN78[2]). The positions of H atoms were determined

Table 1. Final Atomic Parameters (Positional ×10^4) and Equivalent Isotropic Temperature Parameters (B_{eq} ×10) for Non-H Atoms with Their e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}/Å$^{2\,a)}$
C(1)	1064(6)	3705(7)	−347(7)	50(4)
C(2)	881(5)	4001(6)	1659(6)	34(3)
C(3)	2304(6)	4499(9)	2745(7)	62(5)
C(4)	733(5)	4469(6)	3635(5)	36(3)
C(5)	−120(6)	6186(7)	3145(6)	49(4)
C(6)	1126(5)	6164(6)	4585(5)	31(3)
C(7)	1557(6)	7906(7)	5459(7)	54(5)
N(1)	1443(4)	3910(5)	767(5)	41(3)
N(2)	1302(4)	4241(5)	2660(5)	37(3)
N(3)	579(4)	5610(5)	3843(5)	35(3)
N(4)	1035(4)	7265(5)	4635(5)	40(3)
O(1)	24(3)	3883(4)	1594(4)	41(2)
O(2)	1671(3)	5653(4)	5211(4)	41(2)

a) The equivalent temperature parameters are defined by Hamilton.[6]

Table 2. Bond Lengths and Angles

Bond length	l/Å	Bond angle	ϕ/°
C(1)-N(1)	1.466(10)	C(1)-N(1)-C(2)	121.3(6)
C(2)-N(1)	1.345(9)	N(1)-C(2)-O(1)	122.3(6)
C(2)-N(2)	1.377(9)	N(1)-C(2)-N(2)	116.7(6)
C(2)-O(1)	1.241(8)	N(2)-C(2)-O(1)	121.0(6)
C(3)-N(2)	1.475(10)	C(2)-N(2)-C(3)	122.2(6)
C(4)-N(2)	1.455(9)	C(2)-N(2)-C(4)	119.8(6)
C(4)-N(3)	1.422(9)	C(3)-N(2)-C(4)	116.8(6)
C(5)-N(3)	1.482(10)	N(2)-C(4)-N(3)	114.5(6)
C(6)-N(3)	1.364(9)	C(4)-N(3)-C(5)	117.6(6)
C(6)-N(4)	1.342(9)	C(4)-N(3)-C(6)	120.2(6)
C(6)-O(2)	1.250(8)	C(5)-N(3)-C(6)	121.8(6)
C(7)-N(4)	1.465(10)	N(3)-C(6)-N(4)	117.5(6)
		N(3)-C(6)-O(2)	120.7(6)
		N(4)-C(6)-O(2)	121.8(6)
		C(6)-N(4)-C(7)	120.4(6)

from a difference Fourier map. The structure was refined anisotropically for non-H atoms and isotropically for H atoms by a block-diagonal least-squares method. The final R was 0.087 and R_w was 0.082 (w=unit wt) (s=2.3), $(\Delta/\sigma)_{max}$ in final refinement cycle was 0.103 for non-H atoms, max. and min. $\Delta\rho$ in the final difference map were +0.3 and −0.4 e Å^{-3}. The atomic scattering factors were taken from Ref. 3. Calculations were carried out on a HITAC M-680H computer at the Computer Center of The University of Tokyo, using the local version of UNICS III.[4] The final atomic parameters are given in Table 1.[5] Bond lengths and angles are given in Table 2.

Results and Discussion

A view of the molecule with atomic numbering is shown in Fig. 1. O(1), C(2), N(1), and N(2) lie on a plane, which makes an angle of 98° with the other plane composed of O(2), C(6), N(3), and N(4). While two ureido groups are substantially on a plane in TMDMU, forming a ring with a hole of 0.5—1.6 Å, the BDMUM molecule has no such ring structure in the crystalline state. In spite of the difference in the molecular structures of TMDMU and BDMUM, a possible specific interaction with Li^+ or Na^+ was observed for both compounds. K^+, however, was apparently caught by BDMUM, but not by TMDMU. These facts suggest that BDMUM takes a similar structure to TMDMU by capturing alkaline metal ions in solutions, though the former is more flexible to catch metal ions than the latter. The possibility of interactions of metal ions with carbonyl anions can be ruled out. That is, the extent of resonance of the ureido groups in urea,[7] BDMUM, and TMDMU decreases in this order since the C=O bond lengths of these are 1.262, 1.241(8), and 1.250(8), and 1.216 Å respectively, and the C-N bond lengths adjacent to the carbonyl groups are 1.335 Å in urea, 1.342(9), 1.345(9), 1.364(9), and 1.377(9) Å in BDMUM, and 1.377 and 1.378 Å in TMDMU. Even though the differences in the C=O bond lengths are partly due to the presence and absence of the hydrogen bonds involving the C=O bonds (urea has 4, BDMUM has 1 and TMDMU has no hydrogen bonds), the conclusion described above can hold. None of the urea, bis(ureido)methane, and bis(1-methylureido)methane showed any effect on the UV spectra of the solutions of phenol-alkaline metal salts.[1] Thus, interactions between alkaline metal ions and BDMUM or TMDMU are possibly correlated to the localized electron densities of four nitrogen atoms donated by the methyl groups.

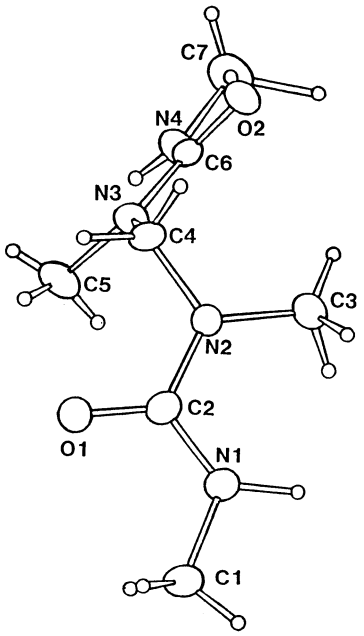


Fig. 1. The view of the molecule with atomic numbering.

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